

VAN DER WAALS INTERACTION OF PARALLEL POLYMERS AND NANOTUBES

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We study the mutual interactions of simple, parallel polymers and nanotubes, and develop a scheme to include the van der Waals interactions in the framework of density functional theory (DFT) for these molecules at intermediate to long-range separations. We primarily focus on the polymers polyethylene, isotactic polypropylene, and isotactic polyvinylchloride, but our approach applies more generally to all simple polymers and nanotubes. From first-principle DFT calculations we extract the electron density of the polymers and their static electric response. We derive explicit expressions for the van der Waals interaction energy under simple symmetry assumptions.

Keywords: Nanotubes; Polymers; van der Waals Interactions; Density Functional Theory.

I. INTRODUCTION

Developing an ab initio understanding for soft-matter problems, such as found both in the biosciences and in carbon-based nanotechnology, represents an important challenge. Density functional theory (DFT) provides, in principle, the necessary materials-theory account but traditional implementations of DFT are insufficient for soft matter [1, 2]. Traditional DFT implementations provide an accurate account of the intra-molecular (intra-material) binding in regions with a high electron density. However, the typical soft-matter problem, like the binding of graphitic and layered materials [3, 4], of polymer matrices [5], and of polyaromatic dimers [6, 7], is defined by regions of sparse electron density. Here traditional DFT implementations provide no consistent account [5, 8, 9, 10] because they lack a description of the van der Waals (vdW) or dispersion forces. This shortfall of traditional DFT has motivated a series of development works by us [2, 3, 6] and by others [11, 12, 13, 14] that seeks a consistent extension of traditional DFT (accurate for intra-molecular binding) with electron-density based calculations of the van der Waals interactions (for the intermolecular binding). We thereby extend traditional DFT in a consistent approach that avoids double counting of the electron interaction effects.

The exchange-correlation energy $E_{xc}[n]$ is a functional of the electron density n and represents the central concept in all DFT approximations. It represents the total electron-electron interaction energy which is not included in the mean-field approximation described by the electron Poisson potential $\Phi(\mathbf{r})$. Together with the external potential V_{ext} , the functional $E_{xc}[n]$ completely determines the general DFT calculational scheme for the total energy

$$E = T_0[n] + \int d\mathbf{r} n(\mathbf{r}) [\Phi(\mathbf{r})/2 + V_{\text{ext}}] + E_{xc}[n] \quad (1)$$

of an interacting soft/sparse or traditional-materials system. The term $T_0[n]$ in (1) is the kinetic energy of a non-interacting system at density n and is in DFT straight forward to calculate as a single-particle Schrödinger equation problem specific to the materials system, as discussed, for example, in Refs. [15, 16]. The functional $E_{xc}[n]$, however, is universal and it is this functional that we seek to improve beyond the traditional local-density and generalized gradient approximations in the investigations for a new van-der-Waals-density functional (vdW-DF) [2, 3, 6, 17].

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In this paper we illustrate the nature of such a new vdW-DF by ab initio and analytical calculations of the intermediate-range interactions between parallel (unbranched) polymers and nanotubes. Specifically, we investigate the interactions between polyethylene (PE), isotactic polypropylene (PP), isotactic polyvinylchloride (PVC), and single-walled carbon nanotubes (CNT). We first determine the structural geometry of the isolated molecules by self-consistent DFT calculations using the generalized gradient approximation (GGA), allowing the atoms to relax to the energetically optimal positions. In the optimization the atoms are moved according to the Hellmann-Feynman forces in the GGA; details of these calculations will be published separately [18]. To this state-of-the-art description of the individual molecular structure we here add a charge-density based description of the intermolecular binding.

The elongated molecules represent an important class of soft-matter interaction problems because they have very anisotropic dielectrical response functions, and as such constitute a special problem. This interaction is naturally separated in three regimes: (i) at binding distances where the van der Waals attraction and kinetic repulsion compete, (ii) the intermediate regime where the local electron density variation is important but where the electron overlap can be neglected, and (iii) the asymptotic regime where the van der Waals interaction is given by the overall (as opposed to the locally varying) susceptibility of the molecules and where traditional van der Waals calculations [19, 20] become feasible. We focus on describing the transition of the molecular van der Waals interactions from intermediate separations and out to asymptotic separations.

The emphasis on intermediate molecule separations d permits us to use a simpler approximative treatment of the anisotropic dielectric response, which we determine upon averaging the electron density along the polymer and nanotube axis. Our aim is to find general trends in polymer-polymer and nanotube-nanotube interactions, and rather than aiming at numerical, very accurate results we here develop analytical, approximate expressions for use in further analyzing the system. More accurate numerical studies, with improved calculations of the molecular dielectrical response, are deferred to a forthcoming paper.

II. THE INTERMOLECULAR VDW BINDING

The vdW interactions involve fluctuating (dipole and multipole) interactions which are naturally expressed in terms of the bare (local-field) and external-field susceptibility tensors, χ_0 and χ_{eff} . Starting from the adiabatic connection formula [21, 22, 23] the dipole-dipole approximation of the exchange-correlation energy of two well separated objects 1 and 2 can be written as [24]

$$E_{xc}^{\text{asympt}}[n] = E_{\text{vdW}}[n] \simeq - \int_0^\infty \frac{du}{2\pi} \int d^3r_1 \int d^3r'_1 \int d^3r_2 \int d^3r'_2 \sum_{a,b,c,d} \chi_{\text{eff},1}^{ab}(\mathbf{r}_1, \mathbf{r}'_1; u) T_{12}^{bc}(\mathbf{r}_1, \mathbf{r}_2) \chi_{\text{eff},2}^{cd}(\mathbf{r}_2, \mathbf{r}'_2; u) T_{21}^{da}(\mathbf{r}_2, \mathbf{r}_1). \quad (2)$$

Here we allow for *anisotropic* effective susceptibility tensors of the objects. The anisotropy must necessarily be taken into account for such extended objects as the straight polymers and nanotubes discussed here. The interaction tensor is given by $T_{ij} = -\nabla_i \nabla_j |\mathbf{r}_j - \mathbf{r}_i|^{-1}$. A standard frequency integration has been turned into an integral on the imaginary axis, with $u = -i\omega$ and ω the physical frequency. Hartree atomic units are used throughout, unless otherwise noted.

In this study we seek only to explore the formal nature of the interactions between parallel polymers and nanotubes. We therefore make use of a simplified but electron-density based model description of the bare molecular susceptibility χ_0 which is assumed diagonal. This model assumption implies that the anisotropic dielectric response χ_{eff} (that characterizes the external-field response of polymers/nanotubes) is taken to arrive exclusively by the local-field effects that are specified by this diagonal χ_0 .

For the diagonal elements of χ_0 we use the approach of Refs. [4, 25], that is, a slightly modified version of the effective susceptibility used in Ref. [19]

$$\chi_0(\mathbf{r}, \mathbf{r}'; u) = \delta(\mathbf{r} - \mathbf{r}') \frac{n(\mathbf{r})}{u^2 + u_0^2}. \quad (3)$$

The valence electron density $n(\mathbf{r})$ is obtained directly from the above-mentioned self-consistent DFT calculations. The cut-off frequency u_0 was introduced in Eq. (3) to avoid an unphysical divergence

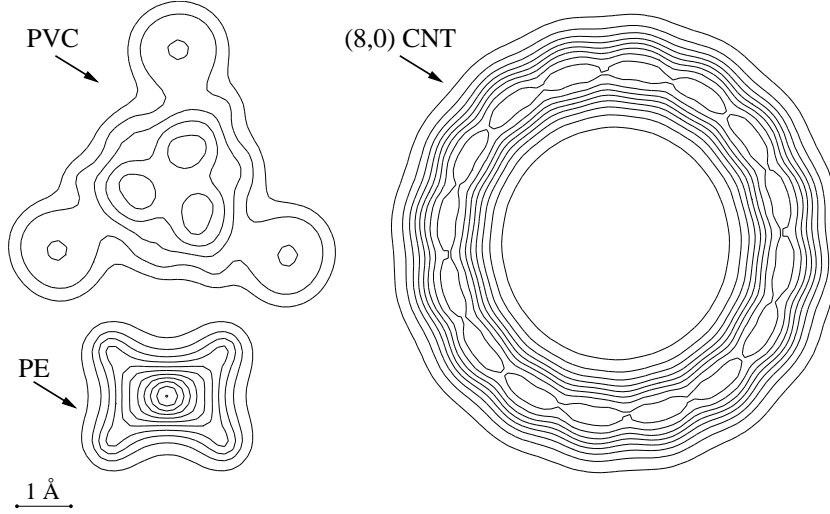


FIG. 1: Valence charge density $n(\mathbf{s})$ of polyethylene (PE), polyvinylchloride (PVC), and the $R_{(8,0)}$ -nanotube (CNT), averaged along the length of the molecules. Contour line spacing is $0.15 \text{ e}\text{\AA}^{-3}$ and only densities equal to or above this value are shown. The valence charge density plot of polypropylene (PP) looks qualitatively similar to that of PVC.

in the static limit ($u = 0$). The cut-off is determined from a separate set of self-consistent DFT calculations that provide results for the static polarization by imposing a finite external electrical field [4, 25] perpendicular to the polymer and nanotube axis.

Figure 1 shows the electron density (averaged along the polymer and nanotube axis) as calculated by traditional DFT for the molecules PE, PVC, and CNT. The averaging along the length is done in the same spirit as our calculations for the vdW interactions in layered materials [2, 3, 17]. The averaging provides a qualitative picture of the electron-density variation that effectively determines the intermolecular vdW interaction at the relevant intermediate molecular separations. For simplicity we choose to base the set of numerical and analytical evaluations of the vdW correction (2) on dielectric-response functions specified by these averaged electron densities.

Figure 1 also suggests that this effective electron distribution has an approximate cylindrical rotational symmetry which we utilize for further simplifications in our present model study. We term such molecules ‘cylindrical’ and these remain the focus of this paper because they offer in several cases comparison against analytical expansions and evaluations. We stress that for the question of the mutual vdW interactions the most relevant measure of cylindrical symmetry is exactly the angle-dependence of the static external field response. In the set of investigated molecules this angle-dependence is small, as shown for PE in the inset of Figure 2(a) from direct evaluation in traditional DFT.

An element of charge at position \mathbf{s} (specified in two dimensions relative to the molecule center-of-mass line) on the molecule responds to the local electric field according to $\chi_0(\mathbf{s}; u)$ given by (3). The local field is the applied electric field $\mathbf{E}_{\text{applied}}(u)$ (which arises from charge fluctuations at the other molecule) screened by the presence of other elements of charge in the neighborhood. The local electric field is described via the local electric potential $\phi(\mathbf{s}; u)$ and given by charge conservation

$$-\nabla \cdot \{(1 + 4\pi\chi_0) \nabla \phi\} = 0. \quad (4)$$

The effective susceptibility tensor χ_{eff} , which appears in the expression for the interaction energy (2), is related to the local susceptibility and the local electric potential by

$$\chi_{\text{eff}}(\mathbf{s}; u) \mathbf{E}_{\text{applied}}(u) = -\chi_0(\mathbf{s}; u) \nabla \phi(\mathbf{s}; u). \quad (5)$$

Due to the assumed translational invariance along the length of the molecule we can in general solve (4) numerically as a two-dimensional differential equation in $\phi(\mathbf{s}; u)$ with the frequency u as a parameter, and thus find $\chi_{\text{eff}}(\mathbf{s}; u)$ from (5). The spatial integral $\alpha(u) = L \int d^2s \chi_{\text{eff}}(\mathbf{s}; u)$ taken at $u = 0$ gives us the molecular, macroscopic susceptibility tensor as a function of u_0 . Comparing

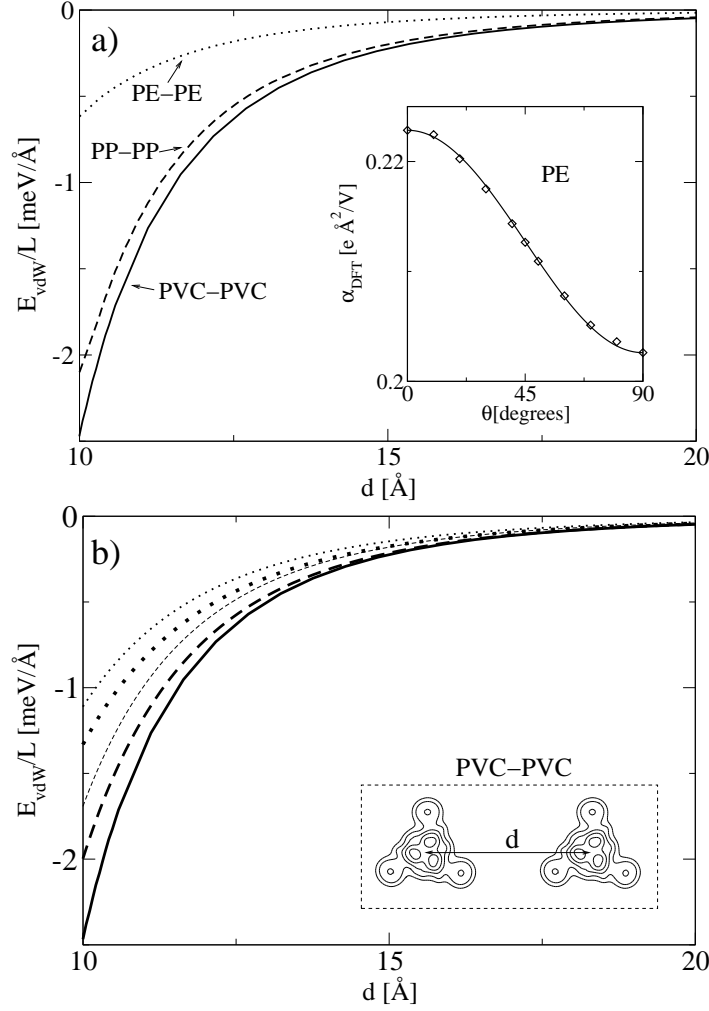


FIG. 2: The van der Waals part of the interaction energy for two parallel polymers at separation d . Panel (a) shows E_{vdW}/L numerically evaluated for sets of length-averaged polymers keeping their full angular structure. The squares in the inset show the DFT calculated susceptibility of PE for different angles. The full line is a fit based on the rotational properties of the susceptibility tensor. Panel (b) shows the results for the vdW interaction energy of PVC in different approximations. The thick lines correspond to evaluations keeping the full angular structure for the length-averaged electron density, and the thin lines correspond to evaluations of the radially averaged density. Shown are expansions to 5th order in d^{-1} (dotted lines), to 7th order (dashed lines), and the full calculation without expansion (solid line). In both panel (a) and (b) the PVC molecules are oriented as shown for separation $d = 10$ Å in the inset of (b). The PP molecules are oriented similarly to PVC, and the PE molecules are oriented with the long axis towards each other.

$\alpha(u=0)$ to the static DFT-calculated molecular susceptibility we determine the frequency constant u_0 .

In polymers our approach [4, 25] yields a value of the static polarization which varies with the angle at which the electric field is applied. However, for the simple polymers the variation is small, as shown for PE in the inset of Figure 2(a). For PP and PVC the susceptibility is almost constant with respect to rotation, with $\alpha^{\text{PP}} = 0.97 \pm 0.01 \text{ e Å}^2/\text{V}$ and $\alpha^{\text{PVC}} = 1.01 \pm 0.01 \text{ e Å}^2/\text{V}$. The values u_0 found for the angular means of the static polarizability are [18] 0.429 Ha for PE, 0.507 Ha for PP, and 0.482 Ha for PVC. In nanotubes u_0 depends on the nanotube radius. However, the variation is small and the macroscopic susceptibility is not very sensitive to this variation. For CNT we thus use the large-nanotube value [25] for all nanotubes, $u_0 = 0.30$ Ha.

In the expression for the van der Waals energy (2) the two spatial integrals along the (density averaged) molecules can be performed analytically [4], but leave a cumbersome integral over the

remaining spatial variables and the frequency. These integrals can be numerically solved, and the results for pairs of parallel polymers are shown in Figure 2(a) for a specific relative orientation of the polymers. The results for other relative orientations will be reported in Ref. [18].

III. INTERACTION ENERGY IN CYLINDRICAL SYMMETRY

Whereas it is possible to numerically evaluate E_{vdW} for a general pair of parallel molecules, such results provide only limited insight into the vdW interaction mechanism. To interpret such numerical evaluations we provide instead analytical results that are possible to derive with our choice of simplified local susceptibility function (3) for cylindrical molecules. When cylindrical symmetry is imposed, the local electric potential ϕ factorizes into $\phi(\mathbf{s}; u) = -|\mathbf{E}_{\text{applied}}(u)|W(s; u)\cos\theta$, where θ measures the angle from the direction of the applied field. Solving (4) then reduces to the one-dimensional problem of finding $W(s; u)$ with u as a parameter. In Ref. [18] the more complex problem of non-cylindrical polymers will be treated in greater detail.

For cylindrical molecules χ_{eff} is diagonal in the cylindrical representation (s, θ, z) [25], and the interaction energy reduces to

$$\frac{E_{\text{vdW}}}{L} = - \int_0^\infty \frac{du}{2\pi} \int_0^\infty ds_1 s_1 \int_0^\infty ds_2 s_2 \sum_{\beta, \gamma=s, \theta, z} \chi_{\text{eff}}^\beta(s_1; u) \chi_{\text{eff}}^\gamma(s_2; u) G_{\beta\gamma}(s_1, s_2) \quad (6)$$

where the geometry factors are

$$G_{\beta\gamma}(s_1, s_2) = \int_0^{2\pi} d\theta_1 \int_0^{2\pi} d\theta_2 \int_{-\infty}^\infty d(z_2 - z_1) [T^{\beta\gamma}(s_1, \theta_1, z_1, s_2, \theta_2, z_2)]^2. \quad (7)$$

The integral over $z_2 - z_1$ [4] and one of the angles in $G_{\beta\gamma}(s_1, s_2)$ can be carried out analytically, but still leads to intractable expressions in the remaining angle, s_1 , s_2 , and d , and the full presentation is deferred.

Our further treatment of the interaction energy expression differs depending on the nature of the molecules considered. On the one hand the polymers considered here are thin (radius ≈ 2 Å) compared to the typical nanotube (radius ≈ 10 Å) and compared to the typical binding separation (≈ 3 –4 Å plus radii of molecules). This means that a large-separation approximation, based on the center-of-mass to center-of-mass distance d , is a better approximation for the polymers than for nanotubes. On the other hand, nanotubes are about the most cylindrically symmetric extended molecules that exist, and the major part of the electron density is concentrated in a thin cylindrical shell, as shown in Figure 1. It is therefore reasonable to approximate the nanotube electron charge density by a weighted radial delta-function. We further approximate the nanotube effective susceptibility tensor by assuming $\chi_{\text{eff}}^s = \chi_{\text{eff}}^\theta$. Below, we pursue these approximations for polymers and for nanotubes. We also show that the two sets of derivations are consistent under relevant conditions.

IV. POLYMER INTERACTION

As argued above, we can explore the polymer interactions in an expansion in powers of d^{-1} . Expanding the geometry factors, writing $G_{\beta\gamma} = \sum_i G_{\beta\gamma}^{(i)} d^{-5-i}$, the first three even-index terms are

$$G^{(0)} = \frac{9\pi^3}{128} N \quad (8)$$

$$G^{(2)}(s_1, s_2) = \frac{225\pi^3}{1024} ((N + 2M)s_1^2 + (N + 2M)^T s_2^2) \quad (9)$$

$$G^{(4)}(s_1, s_2) = \frac{3675\pi^3}{8192} ((N + 4M)s_1^4 + 3Ls_1^2 s_2^2 + (N + 4M)^T s_2^4) \quad (10)$$

with the tensors

$$N = \begin{pmatrix} 19 & 19 & 10 \\ 19 & 19 & 10 \\ 10 & 10 & 12 \end{pmatrix}, \quad M = \begin{pmatrix} 12 & 12 & 8 \\ 7 & 7 & 2 \\ 5 & 5 & 6 \end{pmatrix}, \quad L = \begin{pmatrix} 99 & 73 & 52 \\ 73 & 59 & 28 \\ 52 & 28 & 48 \end{pmatrix}. \quad (11)$$

For cylindrical molecules all terms odd in i for symmetry reasons vanish after integration in (6), the odd-index terms being a measure of the molecular charge anisotropy. The polymers treated here in reality are cylindrical symmetric to a varying degree. We find that for PE interactions the numerical values of the first few odd-index contributions to the energy are indeed small [18].

To lowest order in d^{-1} the interaction energy becomes

$$\begin{aligned} \frac{E_{\text{vdW}}^{(0)}}{L} &= - \sum_{\beta, \gamma=s, \theta, z} G_{\beta\gamma}^{(0)} d^{-5} \int_0^\infty \frac{du}{2\pi} \left(\int_0^\infty ds_1 s_1 \chi_{\text{eff}}^\beta(s_1; u) \right) \left(\int_0^\infty ds_2 s_2 \chi_{\text{eff}}^\gamma(s_2; u) \right) \\ &= - \frac{9\pi^2}{256 d^5} \sum_{\beta, \gamma=s, \theta, z} N_{\beta\gamma} J_{\beta\gamma} \end{aligned} \quad (12)$$

where we have defined the frequency integral

$$J_{\beta\gamma} = \int_0^\infty du \overline{\chi_{\text{eff},1}^\beta(u)} \overline{\chi_{\text{eff},2}^\gamma(u)} \quad (13)$$

given by the spatial integral of χ_{eff}^β

$$\overline{\chi_{\text{eff}}^\beta(u)} = \frac{1}{2\pi L} \int d^3r \chi_{\text{eff}}^\beta(s; u) = \int_0^\infty ds s \chi_{\text{eff}}^\beta(s; u). \quad (14)$$

In the approximation $\overline{\chi_{\text{eff}}^s(u)} = \overline{\chi_{\text{eff}}^\theta(u)}$, used below for nanotubes, we find from (12) the asymptotic contribution to the interaction energy

$$\frac{E_{\text{vdW}}^{(0)}}{L} = - \frac{9\pi^2}{256 d^5} (4 \cdot 19 J_{ss} + 2 \cdot 10 J_{sz} + 2 \cdot 10 J_{zs} + 12 J_{zz}) \quad (15)$$

Using (9) and (10) and the corresponding generalization of (13) and (14) the next order corrections can be similarly expressed.

In Figure 2(b) the d^{-1} -expansion is illustrated along with a numerical calculation that keeps the full angular dependence not assuming any rotational invariance (solid line). The energy is for the PVC-PVC interaction in the relative arrangement shown in the inset. This is the orientation affected the most by the anisotropy of the polymer. The thin dotted line is the lowest order contribution (12) of the expansion. As the next non-vanishing order, d^{-7} , is added the description is improved (thin dashed line). We checked that adding the 9th order did improve the description of the energy slightly, but not significantly at the separations considered here. As a comparison, we also show the d^{-1} -expansion of the full angular calculation: the thick dotted line shows the d^{-5} term, and the thick dashed line includes all orders up to d^{-7} . We note that using the assumption of cylindrical symmetry of PVC does worsen the quality of the evaluation somewhat, but already including a few terms in the d^{-1} -expansion improves the approximations.

V. NANOTUBE INTERACTION ENERGY

For nanotubes a useful simplification of (6) and (7) can be obtained by a different approximation. Rather than using the d^{-1} -expansion, we stress that the nanotube electron density is relatively well described as a weighted radial delta-function located on the nanotube radius R [25]. This leads to the approximation $\chi_{\text{eff}}^\beta(s; u) \approx \overline{\chi_{\text{eff}}^\beta(u)} \delta(s - R)/R$, which decouples the susceptibility factors from the spatial integration, and we find

$$\begin{aligned} \frac{E_{\text{vdW}}}{L} &= - \sum_{\beta, \gamma=s, \theta, z} \int_0^\infty \frac{du}{2\pi} \overline{\chi_{\text{eff},1}^\beta(u)} \overline{\chi_{\text{eff},2}^\gamma(u)} G_{\beta\gamma}(R_1, R_2) \\ &= - \frac{1}{2\pi} \sum_{\beta, \gamma=s, \theta, z} J_{\beta\gamma} G_{\beta\gamma}(R_1, R_2). \end{aligned} \quad (16)$$

This is the expression for the interaction of two parallel nanotubes of radii R_1 and R_2 . The integrals in $G_{\beta\gamma}(R_1, R_2)$ yield, in general, tedious expressions with one remaining angular integral. However, with the introduction of another, numerically small approximation of the effective susceptibility tensor we can carry the analysis of E_{vdW} further with simple expressions.

Assuming that the averaged effective radial and tangential susceptibilities on each molecule are identical, $\overline{\chi_{\text{eff}}^s}(u) = \overline{\chi_{\text{eff}}^\theta}(u)$, then $J_{ss} = J_{s\theta} = J_{\theta s} = J_{\theta\theta}$, $J_{sz} = J_{\theta z}$, and $J_{zs} = J_{z\theta}$. This is a less restrictive approximation than the already modest approximation $\chi_{\text{eff}}^s(s; u) = \chi_{\text{eff}}^\theta(s; u)$ imposed in Refs. [4, 25]. The van der Waals energy per nanotube length then becomes [4]

$$\begin{aligned} \frac{E_{\text{vdW}}}{L} = & -\frac{1}{2\pi} \left\{ J_{ss} (G_{ss} + G_{s\theta} + G_{\theta s} + G_{\theta\theta}) + J_{sz} (G_{sz} + G_{\theta z}) \right. \\ & \left. + J_{zs} (G_{zs} + G_{z\theta}) + J_{zz} G_{zz} \right\} \end{aligned} \quad (17)$$

where $G_{\beta\gamma}$ is implicitly taken in nanotube radii R_1 and R_2 .

In Eq. (17) all the sums of G -terms are of the same form, $G_{ss} + G_{s\theta} + G_{\theta s} + G_{\theta\theta} = 19G_{\text{tot}}$, $G_{sz} + G_{\theta z} = G_{zs} + G_{z\theta} = 5G_{\text{tot}}$ and $G_{zz} = 3G_{\text{tot}}$ where

$$\begin{aligned} G_{\text{tot}}(R_1, R_2) &= \frac{9\pi}{128} \int_0^{2\pi} d\theta_1 \int_0^{2\pi} d\theta_2 \left((R_2 \cos \theta_2 + d - R_1 \cos \theta_1)^2 + (R_2 \sin \theta_2 - R_1 \sin \theta_1)^2 \right)^{-5/2} \\ &= \frac{9\pi^2}{16 d^5} \int_0^{\pi/2} d\xi {}_2F_1 \left(5/2, 5/2; 1; \{(R_2 - R_1)^2 + 4R_1 R_2 \sin^2 \xi\}/d^2 \right). \end{aligned} \quad (18)$$

The second line is a significant simplification which expresses the geometry variation in terms of the hypergeometric function ${}_pF_q$ integrated over the variable $\xi = (\theta_2 - \theta_1)/2$.

For $R_1 = R_2 = R$ also the remaining integral can be carried out, again in terms of a hypergeometric function [26]. We can thus factorize E_{vdW} into one frequency integral $J_{\text{tot}} = 19J_{ss} + 5J_{zs} + 5J_{sz} + 3J_{zz}$ and one spatial integral $G_{\text{tot}}(R, R)$

$$\begin{aligned} \frac{E_{\text{vdW}}}{L} &= -\frac{1}{2\pi} J_{\text{tot}} G_{\text{tot}}(R, R) \\ &= -\frac{9\pi^2 J_{\text{tot}}}{64 d^5} {}_3F_2 \left(1/2, 5/2, 5/2; 1, 1; 4R^2/d^2 \right). \end{aligned} \quad (19)$$

The only numerical integration needed is the frequency integral in J_{tot} . This simplification previously allowed us to extract the graphite-graphite limit of two large-radius nanotubes at intermediate separation [4]. It also allows us to interpret the above-mentioned d^{-1} -expansion of cylindrical molecules: By expanding (19) to the lowest non-vanishing order in d^{-1} we recover (15).

VI. CONCLUSIONS

We have here presented a general approach based on first-principles electron density calculations for computing the intermediate to long-range interactions of parallel, geometrically simple polymers and nanotubes. We have applied the scheme to polyethylene, isotactic polypropylene, and isotactic polyvinylchloride, and the interaction energy for these molecules has been evaluated. We argue that the polymer electron charge density can be approximately described as rotationally invariant, which allows us to derive a number of simple explicit expressions for qualitative insight. For parallel nanotubes we derive expressions for the interactions in terms of hypergeometric functions. Further, the asymptotic expansion for the nanotubes is seen to be consistent with the expression obtained for the cylindrical polymers.

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